NACA RM E54L15

NACA

RESEARCH MEMORANDUM

A METHOD FOR THE ANALYSIS OF COMPOUNDS CONTAINING BORON, CARBON, AND HYDROGEN

By Harrison Allen, Jr., and Stanley Tannenbaum

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

WASHINGTON

March 3, 1955

NACA RM E54L15

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

RESEARCH MEMORANDUM

A METHOD FOR THE ANALYSIS OF COMPOUNDS CONTAINING BORON, CARBON, AND HYDROGEN

By Harrison Allen, Jr., and Stanley Tannenbaum

SUMMARY

The analytical method described in this report was determined for each of the elements, boron, carbon, and hydrogen from the quantitative analysis of a single sample of an organoboron compound. The compound was oxidized quantitatively with oxygen in a steel bomb at high temperature and pressure. Upon completion of the oxidation process, the combustion products, carbon dioxide, water, and hydrated boric oxide were separated by appropriate techniques, and their quantities subsequently determined. From these measured quantities, the percentages of carbon, hydrogen, and boron in the original compound were then calculated.

The proposed procedure was applied successfully to the analysis of several trialkyl borates and trialkyl boranes. Applicability of the method to hydrocarbon analysis was also investigated. Analytical data obtained by the proposed method are presented.

INTRODUCTION

Although several accurate methods for the determination of boron are reported in the literature (ref. 1), no satisfactory method has been proposed for the simultaneous determination of carbon, hydrogen, and boron when all are present in a compound. Analyses of organoboron compounds are usually limited to determinations of boron and, if present, hydrolyzable hydrogen. In such compounds, carbon is difficult to determine accurately by the usual methods, because combustion is incomplete. When the compound contains only the three elements, total hydrogen is sometimes reported by difference, and consequently reflects any errors in the boron and carbon determinations.

A method which provides for the determination of each of the elements, boron, carbon, and hydrogen from analysis of a single sample would have obvious advantages. Such a method is described in this report.

The organoboron compound was oxidized quantitatively with oxygen in a steel bomb at high temperature and pressure. Upon completion of the

oxidation process, the combustion products, carbon dioxide, water, and hydrated boric oxide were separated by appropriate techniques, and their quantities subsequently determined. The percentages of carbon, hydrogen, and boron in the original compound were calculated in the usual manner.

The proposed procedure was tested by analyzing several alkyl borates and alkyl boranes; applicability of the method to hydrocarbon analysis was also investigated.

METHOD

The oxidation bomb is sketched in figure 1. The body of the bomb was made from an Inconel seamless tube which had a 3/16-inch wall thickness. The tube was closed at one end with a 1/2-inch Inconel plate; a grooved stainless-steel flange was welded to the other end. The top of the bomb consists of a mating grooved flange welded to a stainless-steel nipple which, in turn, was welded to a high-pressure valve (the valve was purchased commercially and was repacked with Teflon). A perforated stainless-steel cap was attached (threads) to the top flange below the nipple. The bomb was sealed by squeezing an annealed aluminum gasket between the flanges and held together by six stainless-steel bolts and nuts.

The apparatus for pressurizing the bomb with oxygen before the combustion process, and also for absorbing the carbon dioxide and water vapor after the process is illustrated in figure 2. A U-trap and a simple vacuum line consisting of a mechanical pump, a diffusion pump, a McLeod gage, and appropriate lines and valves were required to collect the liquid water of combustion. A Fisher titrimeter (ref. 2) was used in the potentiometric titration of the boric acid.

Trimethyl and tributyl borates were fractionally distilled in a 3-foot, helix-packed column. Triamyl borate and tripropyl borane were prepared at the Lewis laboratory by distillation in a 6-foot Podbielniak column. Samples of 2,3-dimethylbutane and 2,2-dimethylhexane were obtained from National Bureau of Standards. Triethyl borane, vinyl and isopropyl cyclopropanes having 99.8, 99.8, 99.9 mole percent purity, respectively, were prepared at the Lewis laboratory.

The following reagents were used in the analysis:

Oxygen, (available at pressure of 2000 lb/sq in.), percent purity	99.5
Anhydrone (anhydrous magnesium perchlorate)	c.p.
Ascarite, mesh	8 to 20
Mannitol	reagent grade
Sodium hydroxide (solution standardized against potassium acid phthalate using Fisher titrimeter)	0.2 N

PROCEDURE

A weighed sample (approx. 0.3 g) of the compound contained in a glass ampoule was placed in the bomb. A wad of spun glass wool (to filter out particles of boric oxide when the combustion gases are bled out of the bomb) was placed in the perforated cap attached in position to the top flange. The bomb is closed and attached to the pressurization system as shown in figure 2. It was flushed twice with 10 atmosphere portions of oxygen, then loaded with 25 atmospheres of oxygen and immersed in water to test for leaks. The bomb was then placed behind a safety barrier,[1] and the bottom half of the bomb heated by a Meker gas burner. The heat caused the sample in the glass ampoule to expand and break out into the hot oxygen atmosphere (the explosion of the glass ampoule is audible) and combustion proceeds. Heating was continued for 1/2-hour during which time the end of the bomb took on a dull red glow indicating a temperature of approximately 500° C.

The bomb was cooled to room temperature and the combustion gases contained in it allowed to pass through Anhydrone and Ascarite (fig. 2) which absorbed the water vapor and carbon dioxide, respectively. Flushing twice with 10-atmosphere portions of oxygen removed all the gaseous products from the bomb.

The bomb was attached through a U-trap to a vacuum system and evacuated at room temperature to a pressure of 10^{-6} millimeters of mercury. Any products, volatile at reduced pressure, were allowed to pass into the trap, which was cooled by liquid nitrogen to -196° C. Thus, all the water from the combustion not absorbed by the Anhydrone or combined as a hydrate with the boric oxide remaining in the bomb is collected (see DISCUSSION AND RESULTS).

The evacuated bomb is removed from the vacuum system, and distilled water was allowed to bleed into it as the valve was opened. The bomb was disassembled and the contents thoroughly washed into a 600-milliliter beaker. The cap containing the wad of glass wool was detached from the top flange and placed in the beaker. The solution was then potentiometrically titrated for boric acid with the Fisher titrimeter, according to the method of Blumenthal (ref. 3) which is based on the neutralization of boric acid with sodium hydroxide in the presence of mannitol.

---

[1]The bomb was hydrostatically tested under 2000 pounds per square inch pressure at room temperature; however, since the strength of the bomb is unknown at the temperature and pressure at which the combustion process occurred, the bomb was always heated behind a safety barrier. While more than 50 analyses were made without any bomb failure, it is recommended that the analyst never be exposed to the bomb while it is hot and pressurized.

DISCUSSION AND RESULTS

In order to obtain an analysis for hydrogen, it is necessary to determine the total amount of water formed in the combustion of the sample. This water is present as (a) water vapor, (b) water of hydration chemically combined with boric oxide, and (c) liquid water not combined chemically with boric oxide. The amounts of water vapor and uncombined liquid water can be directly measured by increase in weight of Anhydrone and cold trap, respectively. The amount of water combined chemically, however, must be found indirectly from the quantity of boric oxide determined by titration. This determination can be made, if after evacuation of the bomb at room temperature, the ratio of water to boric oxide is known and reproducible.

The constancy of this ratio was tested experimentally by dehydrating boric acid to anhydrous boric oxide (ref. 4) and then adding a weighed amount of water to the anhydrous oxide. The sample was evacuated at room temperature as described in the section on PROCEDURE. When the pressure was reduced to 10^{-6} millimeter of mercury, the weight of water collected in the cold trap was determined. Data from such experiments (table I) show that the hydrate under these conditions is stable as $B_2O_3 \cdot 3H_2O$ and that all excess water is collected quantitatively in the cold trap.

Application of this analytical method to the analysis of several trialkyl borates, trialkyl boranes, and hydrocarbons gave the data in table II. The method gave results which usually were slightly lower than theoretical. While no definite explanation can be given for this trend, it is believed to represent the summation of losses during the transferring operations employed in the procedure. The error was small, however, and the analyses were sufficiently precise and accurate for most analytical purposes, as is indicated by the standard deviations in table II.

CONCLUDING REMARKS

The method described in this report offers a convenient and rapid procedure for the analysis of the carbon, hydrogen, and boron contained in one sample of an organoboron compound. It has been applied successfully to the analysis of several trialkyl borates and trialkyl boranes. The procedure may prove applicable to the analysis of all types of compound containing boron, carbon, and hydrogen, provided that sufficient hydrogen is present to form water of hydration for all the boric oxide produced in the combustion reaction.

The method is also applicable to the analysis of hydrocarbons and offers possible advantages over the combustion train method in the analysis of (1) volatile hydrocarbons, in which problems are encountered in

weighing and transferring the sample to a combustion train, and (2) polynuclear aromatic compounds which are sometimes difficult to oxidize completely.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, December 7, 1954

REFERENCES

1. DeFord, Donald D., Lucchesi, Claude A., and Thoburn, James M.: Analytical Chemistry of Boron - A Survey of Methods for the Separation, Detection, and Determination of Boron and Boron Compounds. Dept. Chem., Northwestern Univ., Evanston (Illinois), June 1953.

2. Staff of the Development Laboratory of the Fisher Scientific Co.: Manual of Volumetric Analysis with the Fisher Titrimeter. Fisher Scientific Co.

3. Blumenthal, Herman: Determination of Boron in Metal Borides. Anal. Chem., vol. 23, no. 7, July 1951, pp. 992-994.

4. Van Artsdalen, Ervin R., and Anderson, Keith P.: The Molar Heats of Solution of Boric Oxide and Boric Acid. Jour. Am. Chem. Soc., vol. 73, no. 2, Feb. 1951, pp. 579-581.

[redacted]

TABLE I. - LOSS OF EXCESS H_2O FROM $B_2O_3 \cdot XH_2O$ UNDER VACUUM AT ROOM TEMPERATURE TO FORM $B_2O_3 \cdot 3H_2O$ (H_3BO_3)

	Items	Sample 1	Sample 2	Sample 3
1	H_2O added to anhydrous B_2O_3, g	1.4759	0.7021	1.0385
2	H_2O removed from $B_2O_3 \cdot XH_2O$ under vacuum, g	1.2850	0.4859	0.8835
3	H_2O combined with B_2O_3, g (difference between 1 and 2)	0.1909	0.2162	0.1550
4	Calculated amount of H_2O needed to combine with weight of B_2O_3 used, to form $B_2O_3 \cdot 3H_2O$, g	0.1919	0.2184	0.1560
5	Ratio of combined H_2O to calculated $H_2O \times 100$	99.5	99.0	99.4

[redacted]

TABLE II. - ANALYSIS OF VARIOUS COMPOUNDS

Compound	Carbon, percent			Hydrogen, percent			Boron, percent		
	Theoretical	Found	Deviation	Theoretical	Found	Deviation	Theoretical	Found	Deviation
$(C_5H_{11})_3BO_3$	66.17	65.93	0.24	12.22	12.13	0.09	3.97	3.85	0.12
Triamyl borate		65.94	.23		12.10	.12		3.74	.23
		66.10	.07		12.20	.02		3.93	.04
		66.08	.09		12.09	.13		3.92	.05
		65.89	.28		12.30	-.08		3.83	.14
		66.14	.03		12.14	.08		3.84	.13
		66.00	.17		12.23	-.01		3.84	.13
		65.93	.24		12.17	.05		3.75	.22
		65.91	.26		12.10	.12		3.81	.16
Average		65.99	.18		12.16	.06		3.83	.14
$(C_4H_9)_3BO_3$	62.62	62.46	0.16	11.83	11.75	0.08	4.70	4.69	0.01
Tributyl borate		62.50	.12		11.81	.02		4.64	.06
Average		62.48	.14		11.78	.05		4.66	.04
$(CH_3)_3BO_3$	34.67	34.59	0.08	8.73	8.60	0.13	10.41	10.28	0.13
Trimethyl borate		34.59	.08		8.74	-.01		10.35	.06
Average		34.59	.08		8.67	.06		10.32	.10
$(C_2H_5)_3B$	73.53	73.21	0.32	15.43	15.22	0.21	11.04	10.91	0.13
Triethyl borane		73.36	.17		15.34	.09		11.09	-.05
		73.57	-.04		15.39	.04		10.86	.18
Average		73.38	.15		15.32	.11		10.95	.09
$(C_3H_7)_3B$	77.16	76.80	0.36	15.11	14.86	0.25	7.72	7.54	0.18
Tripropyl borane		76.80	.36		14.87	.24		7.56	.16
Average		76.80	.36		14.86	.24		7.55	.17
C_6H_{14} NBS	83.62	83.80	-0.18	16.38	16.36	0.02			
2,3 Dimethyl -butane		83.53	.09		16.31	.07			
Average		83.66	.04		16.34	.04			
C_8H_{18} NBS	84.12	84.33	-0.21	15.88	15.83	0.05			
2,2 Dimethyl -hexane		84.19	-.07		15.80	.08			
Average		84.26	-.14		15.82	.06			
C_5H_8	88.16	87.96	0.20	11.84	11.73	0.11			
Vinyl cyclopropane		87.95	.21		11.76	.08			
Average		87.96	.20		11.74	.10			
C_6H_{12}	85.62	85.28	0.34	14.38	14.22	0.16			
Isopropyl cyclopropane		85.35	.27		14.28	.10			
Average		85.32	.30		14.25	.13			
Standard deviation									
Precision			0.11			0.07			0.07
Accuracy			0.22			0.12			0.14

[redacted]

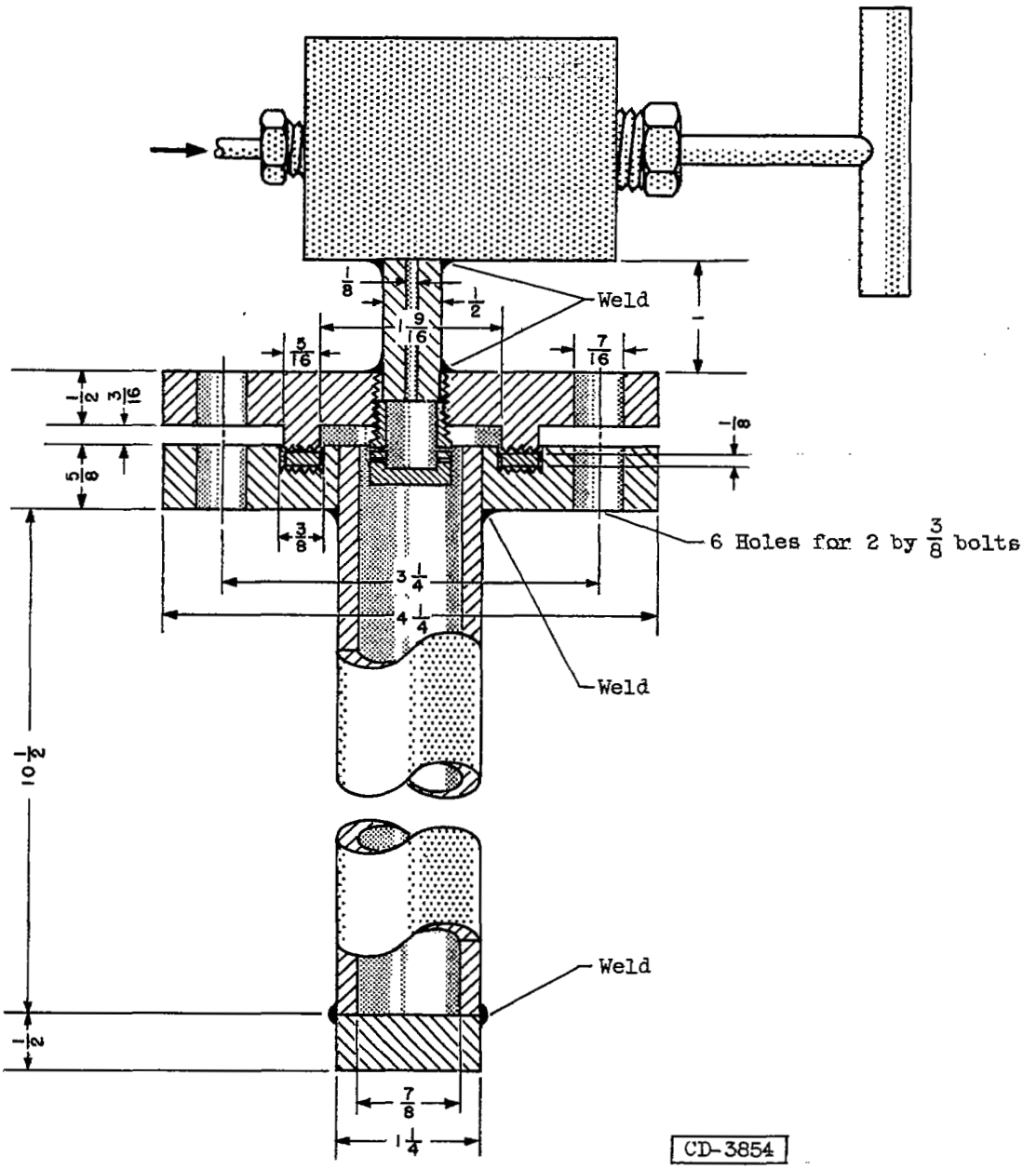

Figure 1. - Oxidation bomb. (All dimensions are in inches.)

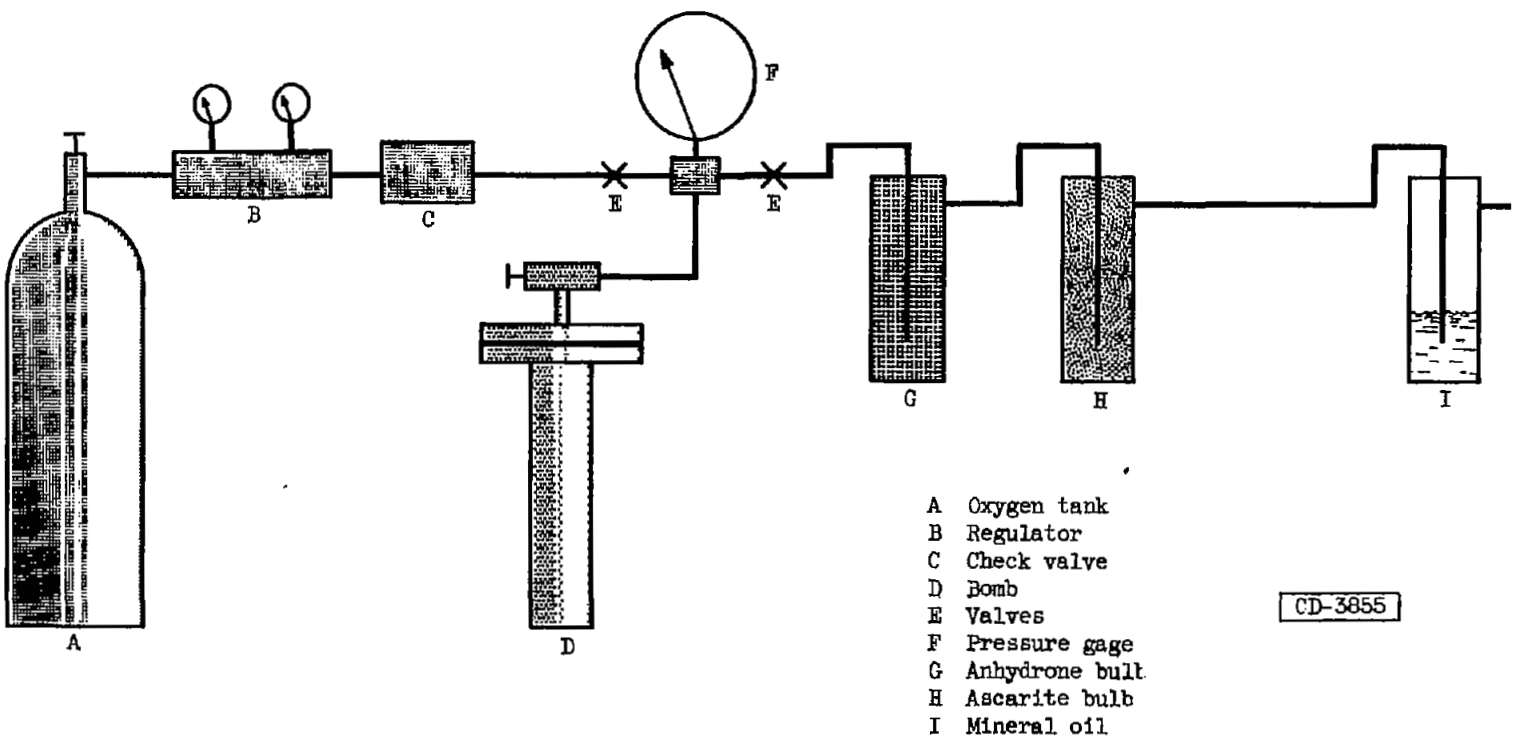

Figure 2. - Oxidation bomb connected to pressurization and absorption systems.